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SUBJECT: ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC
COMPOUND OZONE REACTIVITY. **Part 1. Speciating VOC Emissions using
Confidential Statements of Formula.**

ABSTRACT

This memo describes a Confidential Statement of Formula (CSF)-based speciation/emission potential (EP) estimation procedure. Emission potential refers the volatile fraction of a pesticide product under the conditions of DPR's thermogravimetric analysis method (Marty et al., 2010). The EP is assumed to represent product volatilization under actual use conditions. Speciation refers to identification of the actual chemical species comprising the volatile fraction of a pesticide product. In this paper we document the EP estimation procedure and assess its accuracy by comparing product CSF estimated-EPs to measured-EPs. The volatile components of 134 nonfumigant products reported as used in the 1990 and/or 2007 San Joaquin Valley (SJV) ozone season pesticide volatile organic chemical (VOC) inventory were identified using product CSFs and an empirical vapor pressure (VP) cutoff. The total percentage of estimated volatiles in each product was then compared to TGA-measured EPs. The VP_{25C} cutoff (vapor pressure at 25C) that yielded the best agreement between estimated and measured EPs was approximately 0.05 Pa. Components with $VP_{25C} > 0.05$ Pa were classified as volatile, while those with $VP_{25C} < 0.05$ were classified as nonvolatile. A paired t-test demonstrated a small but significant bias in estimated EPs relative to measured values. The mean difference between measured and estimated EPs (TGA-measured EP - CSF-estimated EP) was +1.4% ($p=0.003$), the measured TGA EPs being greater. This difference was attributable to inadequate or inaccurate product composition information in most cases. For some products, composition data for the concentrated manufacturing use products (MUP) used to formulate end use products (EUP) was not available. The net effect was a low bias in CSF-estimated EPs because unidentified volatile components in the MUP (e.g. solvents) were not accounted for in the EUP CSF. However, the CSF-estimation procedure also identified products where TGA-measured EPs were substantially in error. This occurred when water was present in the liquid MUP used to formulate the EUP, but was not accounted for in the EUP TGA data submission. When this happens, the water volatilized during TGA analysis is incorrectly assumed to be a VOC and the TGA-measured EP is too high. An additional source of TGA error was due to the absorption of

water by clays or other hygroscopic materials in certain dry EUPs, again causing an upward bias in the TGA-measured EPs. In spite of the deviations between TGA-measured and CSF-estimated EPs, overall the agreement between the two was good. Regression of estimated EPs on measured EP yielded a slope not significantly different than one (slope = 1.02; 0.99, 1.05; 95%CI) with an R^2 of 0.985. Recommendations include CSF analysis of additional products with the goal of refining the 0.05 Pa VP_{25C} cutoff, and more consistent use of CSFs in evaluating TGA data and correcting questionable data. Finally, the CSF analysis provides a method to estimate the composition of pesticide product volatile components, thereby supporting eventual incorporation of reactivity into the VOC inventory.

1. INTRODUCTION

The current pesticide volatile organic compound (VOC) inventory is a mass-based inventory that tracks pounds of VOCs emitted from agricultural and commercial structural pesticide applications. The inventory does not account for differences among VOCs in their ability to participate in ozone forming reactions, i.e. their "ozone reactivity". DPR recently proposed a pilot study to examine how ozone reactivity could be incorporated into the pesticide inventory (Oros, 2009). The objective of the study is to quantify the relative ozone reactivity of individual pesticide products. In estimating relative ozone reactivity, the first step is identify the composition of a product's volatile emissions (speciation). The second step is then to determine the product's relative ozone formation potential using individual component reactivity data. These reactivity data may include Maximum Incremental Reactivity or Equal Benefit Incremental Reactivity data, among others (Carter, 1994). This memorandum

- describes a method for speciating emissions using pesticide product CSFs,
- compares CSF-estimated and TGA-measured-EPs for several high VOC contributing products, and
- documents potential problems that arose when estimating VOC speciation using CSF data.

2. METHODS

A. Compilation of CSFs

The CSFs for pesticide products typically contain the following information: chemical name, source product name, Chemical Abstracts Service (CAS) registry number, purpose in formulation (e.g., inert or active ingredients), and percentage by weight of the chemical in the formulated product. Individual chemicals listed in CSFs are primarily classified as either active ingredients or inert ingredients. The Code of Federal Regulations (CFR), 40 CFR Part 180 (sections 180.910 – 180.960) outlines inert ingredients that the US Environmental Protection Agency (USEPA) has approved for use in pesticide products (<http://www.epa.gov/opprd001/inerts/lists.html>), and these "inerts" are used in pesticide products in California. The Department of Pesticide Regulation

(DPR) lists over 981 active ingredients and 13,417 pesticide products for use here in California (<http://www.cdpr.ca.gov/docs/label/actai.htm>, data accessed 24 Dec 2009).

For this pilot study, registrant-submitted CSFs were compiled for the top nonfumigant VOC-emitting EUPs in the San Joaquin Valley in each of 2 years: the 1990 base year and 2007. When available, CSFs were also obtained for the MUPs used to formulate the EUPs. In total, CSFs were compiled for a total of 84 distinct California-registered products. The products (including their subregistrations and label revisions, as explained later) corresponded to 58 % and 60% of San Joaquin Valley (SJV) adjusted nonfumigant ozone season emissions in 1990 and 2007, respectively.

B. Classification of Product Components

Many pesticide products use the same chemical ingredients. These can function as an active ingredient, anti-caking agent, anti-foaming agent, dye, emulsifying agent, odorant, solvent, surfactant, or thickener. Except for solvents, most of these ingredients have low volatility. Many, such as surfactants, have high molecular weight and very low VPs. Such components are not expected to contribute significantly to tropospheric VOCs.

Active Ingredients: An active ingredient is any substance or group of substances that prevents, destroys, repels or mitigates any pest, or that functions as a plant regulator, desiccant, defoliant, or nitrogen stabilizer.. End use nonfumigant pesticide products are often formulated from manufacturing use products (MUP). MUPs usually contain a high percentage of active ingredient. and may consist of the technical grade of active ingredient only, or may contain inert ingredients, such as solvents or stabilizers, etc. that serve different functions in the product formulation. Most active ingredients are not sufficiently volatile to contribute to tropospheric VOCs due to their high molecular weight and low VPs.

Antifreezes: Antifreezes are used to prevent freezing of a pesticide product. Common antifreeze agents used in pesticide products are ethylene glycol and propylene glycol.

Emulsifying/Dispersing Agents: Emulsifiers have a hydrophobic and a hydrophilic end, which act by surrounding an immiscible molecule, including oils, and forming a protective layer keeping the molecules from clumping together. Dispersing agents are used to keep an emulsion well dispersed. Emulsifier and dispersing agent compositions can include very large polymers of high molecular weight and low VP.

Odorants: Odorants are used as volatile indicators due to their distinctive odor and volatility. An odorant commonly used in pesticide products is methyl salicylate also known as wintergreen. The VP₂₅ of methyl salicylate is comparable to some solvents.

Oils: Oils such as mineral oil and soybean oil generally function as solvents. Mineral oil is composed mainly of alkanes (typically 15 to 40 carbons) and cyclic paraffins, while soybean oil is composed mainly of unsaturated fatty acids including oleic acid (C_{18:1}),

linoleic acid (C_{18:2}), linolenic acid (C_{18:3}). Oils are composed of a range of high molecular weight components that generally have low VPs.

Solvents: Organic solvents are liquids that are used to dissolve active ingredients. Examples of several solvents approved by USEPA for use in pesticide products include: methyl isobutyl ketone, cyclohexanone and N-methyl-pyrrolidinone. Most solvents are volatile enough to contribute to tropospheric VOCs based on their low molecular weight and high VPs.

Solvent Mixtures: Solvent mixtures (e.g. aromatic 100, aromatic 150, aromatic 200) are also used in pesticide products. Aromatic solvent mixtures are generally distillation cuts with a range of volatile components and VPs. The major difference between the aromatic solvent mixtures is carbon number., which increases with distillation range. For instance, aromatic 100 is largely composed of C₉₋₁₀ dialkyl and trialkylbenzenes, aromatic 150 is composed largely of C₁₀₋₁₁ alkylbenzenes and aromatic 200 includes C₁₀₋₁₄ alkylnaphthalenes (Table 1).

Table 1. General composition and approximate component vapor pressures (VPs) of aromatic product solvent mixtures ^A				
	aromatic 100	aromatic 150	aromatic 200	mean VP of chemical class
Total Aromatics (%)	>99.5%	>99.5%	>99.5%	Pascals/(N) ^B
CHEMICAL CLASS				
alkylbenzenes				
C8	~5-10%	<5%	<5%	924/(4)
C9	80%	<5%	<5%	328/(8)
C10	10%	58%	<5%	118/(17)
C11	<5%	12%	<5%	46/(4)
indanes/THN ^C	<5%	14%	6%	26/(4)
alkylnaphthalenes				
C10	<5%	11%	<5%	24/(1)
C11	<5%	<5%	52%	5.8/(2)
C12	<5%	<5%	20%	2.4/(4)
C13	<5%	<5%	8%	0.9/(2)
^A Composition data: Krenek and Rhode, 1988; Vapor pressure data: Syracuse Research Corporation Environmental Fate Database, http://www.syrres.com/eSc/efdb.htm ; USEPA SPARC http://www.epa.gov/Athens/learn2model/part-two/onsite/sparcproperties.htm (SPARC references - Hilal et al., 2003a, 2003b) ^B N = Number of chemicals in class used to calculate mean ^C Tetrahydronaphthalenes				

Surfactants: Surfactants aid in suspending the active ingredient when the product is mixed with a solvent. When applied in the field, surfactants may also allow easier spreading of a product by lowering the surface tension of the liquid. Surfactants are typically high molecular weight, amphoteric and possess very low or no volatility.

Other Agents: Carriers (e.g., clays, fruit pulp, crushed corn cobs, etc.), thickeners, anti-caking agents, anti-foaming agents, preservatives, and dyes are also used in non-fumigant products. Most are used in low amounts in pesticide products and generally have high molecular weight and low VPs.

C. Analysis of Vapor Pressure for Determining Volatility

Vapor pressure at 25C (VP_{25C}) was used to discriminate between chemicals that did or didn't volatilize under the experimental TGA conditions.

Vapor pressure: The pressure of a vapor in equilibrium with a condensed phase (liquid or solid). While VPs vary with temperature, we used to each chemical's VP at 25°C as a relative measure of a chemical's tendency to vaporize at the TGA temperature of 115C.

VP_{25C} data were collected from various databases accessible via the worldwide web including the European Union's Footprint Pesticide Properties Database (<http://sitem.herts.ac.uk/aeru/iupac/index.htm>), California Air Resources Control Board's Consumer Product Solvent Database (http://www.arb.ca.gov/db/solvents/all_cmpds.htm), and Syracuse Research Corporation's Interactive Physical Properties Database (<http://www.syrres.com/what-we-do/databaseforms.aspx?id=386>). Because vapor pressure are sometime variable, we compared database values with published literature data where necessary to identify an accurate VP₂₅ for each chemical.

The VP_{25C} of common chemicals included in high use pesticide products from 1990 and 2007 years are shown in Table 2. From the data it is obvious that solvents generally have much higher VP_{25C} than most active ingredients. In a few cases the VP_{25C} of some nonfumigant active ingredients are comparable to those of low volatility solvents.

Table 2. Vapor pressures of common chemicals included in high use pesticide products from 1990 and 2007.

Chemical Name	CAS	VP at 25°C (Pa) unless noted	VP Reference
<u>Active Ingredients</u>			
Pebulate	1114-71-2	12	SRC
EPTC	759-94-4	3	SRC
Butylate	2008-41-5	2	SRC
Molinate	2212-67-1	0.7	SRC
Phorate	98-02-2	0.11	IUPAC
Naled	300-76-5	0.03	SRC
Diazinon	333-41-5	0.012	SRC
Trifluralin	1582-09-8	6.1E-03	SRC
Methamidophos	10265-92-6	4.7E-03	SRC
Metolachlor	51218-45-2	4.2E-03	SRC
Oxydemeton-methyl	301-12-2	3.8E-03	SRC
Alachlor	15972-60-8	2.9E-03	SRC
Chlorpyrifos	2921-88-2	2.7E-03	SRC
Dimethoate	60-51-5	2.5E-03	SRC
Thiram	137-26-8	2.3E-03	SRC
Metalaxyl	57837-19-1	7.5E-04	SRC
Fenpropathrin	39515-41-8	7.3E-04	SRC
Tribufos	78-48-8	7.1E-04	SRC
Ethofumesate	26225-79-6	6.5E-04	SRC
Methidathion	950-37-8	4.5E-04	SRC
Azinphos-methyl	86-50-0	2.1E-04	IUPAC
Carbaryl	63-25-2	1.8E-04	SRC
Prometryne	7287-19-6	1.7E-04	SRC
Fenamiphos	22224-92-6	1.3E-04	SRC
Dicofol	115-32-2	5.3E-05	SRC
Oxamyl	23135-22-0	5.1E-05	IUPAC
Propargite	2312-35-8	4.0E-05	SRC
Fluazifop-p-butyl	79241-46-6	3.3E-05	SRC
Oxyfluorfen	42874-03-3	2.7E-05	SRC
Endosulfan	115-29-7	2.3E-05	SRC
Napropamide	15299-99-7	2.3E-05	SRC
Sethoxydim	74051-80-2	2.1E-05	SRC
Carboxin	5234-68-4	2.0E-05	SRC
2,4-D	94-75-7	1.9E-05	IUPAC
Cyanazine	21725-46-2	1.8E-05	SRC
Ethephon	16672-87-0	1.3E-05	SRC
Permethrin	52645-53-1	2.9E-06	SRC
Thiabendazole	148-79-8	5.3E-07	SRC
Cypermethrin	52315-07-8	4.1E-07	SRC
Clethodim	99129-21-2	3.5E-07	SRC
Esfenvalerate	66230-04-4	2.0E-07	SRC
Endothal	145-73-3	2.1E-08	SRC
Gibberellic Acid	77-06-5	1.7E-11	SRC

Table 2. Continued

Chemical Name	CAS	VP at 25°C (Pa) unless noted	VP Reference
<u>Solvents</u>			
Methanol	67-56-1	16,932	SRC
Ethanol	64-17-5	7,906	SRC
Isopropyl alcohol	67-63-0	6,053	SRC
Toluene	108-88-3	3,786	SRC
Water	7732-18-5	3,173	SRC
Methyl isobutyl ketone	108-10-1	2,653	SRC
1-Methoxypropanol	107-98-2	1,667	SRC
Aromatic 100	64742-95-6	1,653	CARB
Monochlorobenzene	108-90-7	1,600	SRC
Ethylbenzene	100-41-4	1,280	SRC
p-Xylene	106-42-3	1,179	SRC
Cyclohexanone	108-94-1	577	SRC
Aromatic 150	64742-94-5	480	CARB
Kerosene	8008-20-6	387 (20°C)	CARB
1,2,4-Trimethylbenzene	95-63-6	280	SRC
d-Limonene	5989-27-5	264	SRC
Stoddard solvent	8052-41-3	133	CARB
Hexanol	111-27-3	124	SRC
2-Butoxyethanol	111-76-2	117	SRC
Cyclohexanol	108-93-0	107	SRC
Butyrolactone	96-48-0	60	SRC
Propylene glycol	57-55-6	17	SRC
Naphthalene	91-20-3	11	SRC
Aromatic 200	68477-31-6	5 (20°C)	ExxonMobil
Triacetin	102-76-1	0.3	SRC
Methyl oleate	112-62-9	0.0008	SRC
<u>Other Ingredients</u>			
Ethylene glycol	107-21-1	12	SRC
Methyl salicylate	119-36-8	5	SRC
Butylated hydroxytoluene	128-37-0	1	SRC
Glycerol	56-81-5	0.02	SRC

CARB. California Air Resource Board, Consumer Product Solvent

Database. Web site- http://www.arb.ca.gov/db/solvents/all_cmpds.htm

ExxonMobil Chemical. Website-

<http://www.msds.exxonmobil.com/psims/psims.aspx>

IUPAC. Pesticide Properties Database accessed via IUPAC Portal.

Website- <http://sitem.herts.ac.uk/aeru/iupac/index.htm>

SRC PhysProp Database. Syracuse Research Corporation. Website-

<http://www.syrres.com/what-we-do/databaseforms.aspx?id=386>

Abbreviations: AI is active ingredient and VP is vapor pressure

D. Speciation and Estimation of Emission Potential

Speciation: Speciation refers to identification of the actual composition of the VOCs emitted from a pesticide product. The purpose of this study was to create a robust method for speciating VOCs from a pesticide product by using the product's confidential statement of formula (CSF). Table 3 illustrates a simplified CSF, including percent composition (%) of chemical ingredients (active and inerts) and their purpose in the formulation.

Table 3. Example CSF for a nonfumigant pesticide product		
Chemical	Purpose	Percent by Weight (%)
A	Active Ingredient	10
B	Solvent	45
C	Emulsifier	2
D	Antifreeze	2
E	Water	40
F	Dye	1

Emission Potential: Emission potential refers to the fraction of a product that is assumed to contribute to atmospheric VOCs. In this study, product EPs were estimated by summing the weight percent of all volatile organic components (VOCs). For example, in Table 3 if ingredient B, a solvent, is identified as the only VOC in the product then the product EP is 45%, which is the weight percent (%) of ingredient B in the product. As a second example, if ingredients A and B are both identified as VOCs, then the product EP is 55%, the sum of weight percents (%) of ingredient A (10%) and ingredient B (45%). Thus, the problem of estimating product EPs from CSF data reduces to determining which chemicals are volatile and which are not. This issue is addressed in the next section.

E. Thermogravimetric Analysis (TGA)

The potential for solid or liquid-based pesticide products to emit VOCs is estimated by TGA (DPR, 1994). DPR generally requires registrants to provide TGA analysis for newly registered liquid products. During TGA, pesticide products are heated in an environmentally controlled chamber and held isothermally until the rate of sample mass loss drops below a defined threshold. The mean of three replicate measurements is used to estimate a product EP. The TGA method uses a final holding temperature of 115°C (239°F) to facilitate volatilization and loss of water contained in a pesticide formulation.

The 115°C temperature has been criticized because ambient temperatures in agricultural areas where pesticides are applied are much lower. However, volatilization of chemicals depends on *both* temperature and time. In TGA, a relatively high temperature is used in conjunction with a very short testing interval. The 115°C TGA test regimen has a maximum duration of only 80 minutes. In contrast, actual volatilization of nonfumigant pesticides in the field occurs over characteristic time periods of weeks to month(s) (Ross et al., 1989; Seiber and McChesney, 1988; Seiber et al., 1991; Yates, 2006a; Yates, 2006b; Taylor and Glotfelty, 1989 and numerous references there-in). The high

temperature used in the TGA test offsets the short test duration. Longer laboratory test periods would be experimentally difficult, if not impossible. The 115°C/80 minute maximum test TGA test regimen was determined based on a response surface analysis of different temperature/time combinations across a series of pesticide products. Details on the development of the TGA method for pesticides, method validation and inter-laboratory comparisons are described in Marty et al. (2010).

Carter and Malkina (2007) reported that ozone reactivities of chemicals with VP down to approximately 0.01 Pa may be effectively studied under laboratory conditions, and further suggest that such chemicals are likely to participate in gas phase reactions in the environment. As shown later, a comparison of product CSFs and TGA-measured EPs supports 0.05 Pa as a VP cutoff for distinguishing volatile product components *under experimental TGA conditions*. However, few products examined here had components with $0.01 \text{ Pa} < \text{VP} < 0.1 \text{ Pa}$. Consequently, 0.05 Pa is an approximate cutoff, and additional product analyses is desirable to refine that cutoff value.

DPR currently assumes that volatilization under the short duration - high temperature TGA regimen approximates actual volatilization over the longer time intervals in the field. However, there is some evidence that a lower VP cutoff may be applicable for defining actual volatility in the environment. A recent paper prepared on behalf of the European Crop Protection Association evaluated 24 hr volatilization data from 190 experiments carried out with 80 crop protection chemicals (Guth et al., 2004). These studies were carried out to meet pesticide registration regulatory requirements. Based on those data, Guth et al. (2004) identified approximate lower VP limits of 0.001 Pa for volatilization from soil, and 0.0001 Pa for volatilization from crops. Below these limits they concluded “no noticeable volatility” is expected. Thus, the 0.05 Pa cutoff for identifying volatile components under TGA conditions may yield a low-biased estimate of actual post-application volatilization as it occurs in the field.

3. COMPARISON OF CSF-ESTIMATED EMISSION POTENTIALS AND TGA-MEASURED EMISSION POTENTIALS

A. Comparison of CSF-estimated EPs and TGA-measured EPs

In the absence of data demonstrating otherwise, DPR’s presumption is that the composition of all products that share the same primary EPA registration number are substantively the same. Consequently DPR assigns EPs determined for one product to all of its related sub-registrations and label revisions. In this study CSFs were estimated for a total of 84 distinct California-registered products with TGA measured EP data from the 1990 and 2007 SJV VOC inventories. Some products were used in both years, and a few of the 84 products were related label revisions or subregistrations. Consequently the 84 products represented 79 distinct EPA primary registration numbers ("Primary Registrant Firm Number - Label Number"). Most of the primary registration numbers represented at least 2 label revision or subregistered products that had been or were currently registered in California. Consequently the total number of (active and inactive) California products

represented by the 79 distinct EPA primary registration numbers was 215. Of these, a total of 148 products were in one or both of the 1990 and 2007 inventories. The 148 products account for 58% and 60% of SJV adjusted nonfumigant ozone season emissions in 1990 and 2007, respectively. To estimate the EP from CSF data, the VP_{25C} of individual product components in each CSF were compiled. Components with VP_{25C} > 0.05 Pa were classified as volatile and their weight percent in the product summed to yield the CSF-estimated product EP.

In our initial comparisons, there were large differences (>10%) between CSF-estimated EPs and TGA-measured EPs in some cases. Most of these were attributable to unknown components in the EUP. A principal source of the unknowns was the MUPs used to formulate the EUPs. We were able to obtain MUP CSFs from the original product chemistry registration data submissions for approximately half of the cases and use these to identify the unknown components. Several of the unknowns were volatile solvents in the MUP that were subsequently added to the EUP during the manufacturing process. For these the CSF-estimated EPs were modified accordingly. In a few other cases, the unknown components turned out to be water. Because this water was not reported on the EUP CSF, the measured TGA was not properly corrected for the presence of this water in the original data submission. Consequently the TGA determination was inaccurate (high-biased). For the sake of comparisons here, water was treated as a VOC in the EP estimation procedure for these products. However, product EPs for all subregistered and label revision products of these primary registrations will be corrected in future inventory calculations and in subsequent reactivity calculations (Oros and Spurlock, 2010).

For seven other primary registration numbers where unknown components were > 4% of the EUP, the MUP CSFs could not be located. While some of these yielded relatively good agreement between CSF-estimated and TGA-measured EPs, others showed marked deviations - likely due to unidentified solvents in the MUPs used to formulate the EUPs. All seven were excluded from subsequent analysis to reduce the uncertainty in CSF-estimated EPs and to provide a consistent basis dataset for comparison of the two EP methods. Thus, the final basis data set consisted of 72 primary registration numbers representing 200 total products, of which 134 were in one or both of the 1990 and 2007 inventories. These 72 primary registration numbers represented 45% and 54% of SJV adjusted nonfumigant ozone season emissions in 1990 and 2007, respectively.

Based on a t-test of paired differences between measured and estimated EPs (difference = TGA measured EP - CSF estimated EP), there was a small but significant difference between estimated EPs and the measured values (paired t-test, p=0.003). The mean difference between measured and estimated EPs was 1.4%, the TGA EPs being greater. There were two causes for these differences: error in the CSF-estimation procedure and error in the experimental TGA determinations. In the CSF estimation procedure there were numerous products with small amounts of unknown components, even after censoring those products with > 4% unknowns. In the case where these are volatile, the resultant CSF-estimated EPs were low-biased. However, when water is present as an unknown in the MUP, either due to introduction in the MUP or absorption by hygroscopic materials such as clays, the TGA value will be high-biased. We have

observed several products in this study and elsewhere that contain bentonite, kaolin or other finely-divided high surface area materials, and that also yield non-zero EPs even though they contain no volatile organic chemicals. For example, a recent FTIR analysis analysis of TGA emissions from six sulfur products concluded that the observed mass loss was attributable to water (McConnell et al., 2008). The result of this artifact is a high-bias in TGA-measured EPs.

Finally, there is evidence that DPR's basic assumption, that "the composition of all products that share the same primary EPA registration number are substantively the same" may not always be true. For example, one primary EPA registration number had two CSFs submitted at different times that differed substantially in percentage of volatile solvent and other components. Composition differences between products that share the same primary EPA registration number will be especially problematic in situations where the CSF of one is compared to the TGA data for another.

Overall the agreement between estimated and measured EPs was quite good, with the 5th - 95th percentile range of (TGA measured EP - CSF estimated EP) of -3% to 7% (Figure 1). A regression of CSF-estimated EPs on TGA-measured EPs yields a slope that is not significantly different than one (0.99, 1.05; 95%CI; Figure 2). We conclude that pesticide emissions under TGA conditions can be accurately speciated using CSF analysis. It's also apparent that TGA and CSF analysis are complementary, and both should be used to derive product emission potentials.

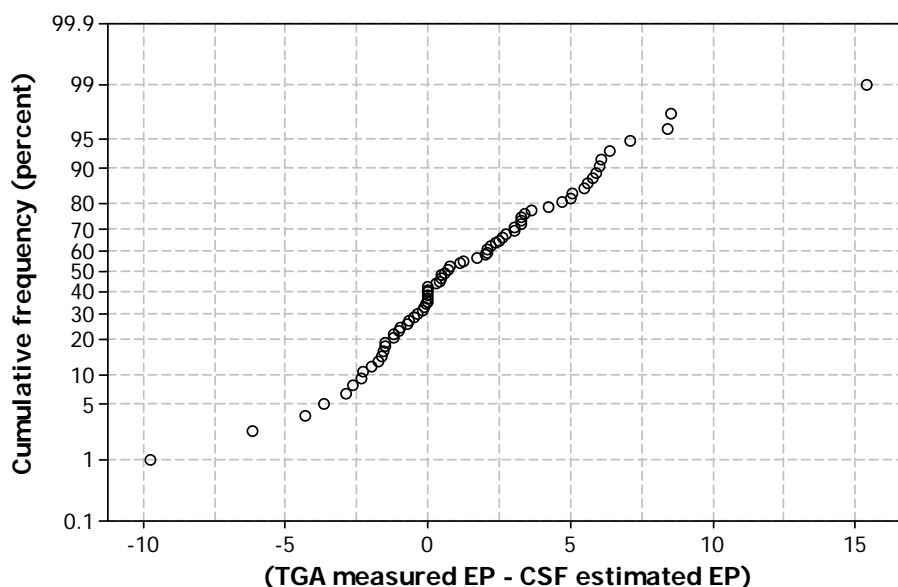


Figure 1. Cumulative frequency of (TGA measured EP - CSF estimated EP) for data compiled for 72 primary registration numbers.

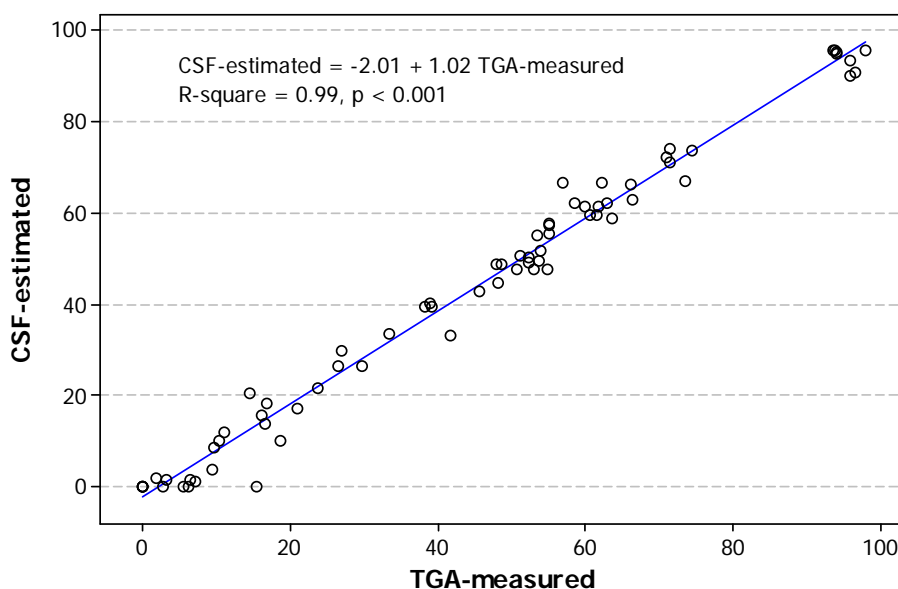


Figure 2. Regression of CSF-estimated EPs on TGA-measured EPs based on data compiled for 72 primary registration numbers.

4. CONCLUSION

In summary, a simple vapor pressure cutoff was used to distinguish "volatile" and "nonvolatile" product components under TGA conditions using product CSFs. While a few issues arose in compiling and analyzing the data, we anticipate these will be easily resolved as CSF analysis becomes routine. The problems included:

- difficulty obtaining complete composition data for some EUPs. One principal cause was difficulty in locating CSFs for MUPs used to formulate EUPs. In some cases this resulted in our inability to identify all volatile components in a product.
- difficulty locating product CSFs for older products where the primary registrant had sold the product or if the company re-organized.
- lack of composition data for proprietary mixtures such as certain surfactants and emulsifiers; these sometimes contain unidentified VOC components. While the total VOC contribution from such mixtures is relatively low in comparison to other pesticide product components (i.e. generally $\ll 5\%$), they are a potential source of error when using CSFs to estimate EUP EPs.

The accuracy of the CSF-based EP estimation/speciation procedure was demonstrated using data compiled for 72 EPA registration numbers representing 134 products reported as used in the 1990 and/or 2007 San Joaquin Valley pesticide VOC inventories. Regression of CSF-estimated EPs on TGA-measured values yielded a slope not significantly different than one with a correlation coefficient $r > 0.99$ ($p < 0.001$). A small bias was observed, with the mean of [TGA-measured EP - CSF-estimated EP] of +1.4%

(*paired t-test*, $p=0.003$). This bias was attributable to incomplete product composition information for some products. However, the bias is comparable to the error in TGA analysis of some products. For example, formulations containing finely-divided hygroscopic materials such as clays may absorb water, leading to errors in TGA measured EPs.

In spite of the small bias, these data support the use of CSF analysis in both review of TGA data and for speciating TGA emissions. Detailed CSF analysis should be viewed as complementary to the TGA EP determination method. There were a number of cases where problems or errors in the TGA determination became evident after review of product CSFs. Use of both TGA and CSF data to determine EPs will improve the accuracy of the inventory.

In most cases, CSF analysis allowed clear and unambiguous speciation of volatile components in pesticide products under TGA conditions. We recommend conducting further paired comparisons of CSFs and TGA data to refine our current 0.05 Pa vapor pressure cutoff used to classify components as to "volatile" or "not volatile" under TGA conditions.

5. REFERENCES

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